The Mechanism of the Mutual Precipitation of Hydrosols.

By

LUCILLE JOHNSON, A.B., M.A.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science
in Columbia University

NEW YORK CITY
1923

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To My Father and Mother

ACKNOWLEDGMENT

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L. J.

INTRODUCTION

Among the interesting properties of colloidal substances is the tendency of certain sols to precipitate when mixed, and the apparent indifference of other sols to each other. Linder and Picton[1] (1897), when studying this mutual reaction with some care, found that it varies from a mere coarsening of the particles to complete precipitation, and that the precipitating sols migrated oppositely in an electrical field. This was well in accord with the tendency of acid and basic dyes, which are usually colloidal in nature, to aggregate, and for the particles to migrate in an electrical field in the direction of the migration of the dye in excess.

Lottermoser[2] (1901) attempted to prepare mixed gels by mixing sols and adding electrolytes to coagulate the mixture. Frequently precipitation resulted before the electrolyte was added, and a table of the incompatible sols was found to be the same as a table for the migration of the sols in an electrical field, from which it was concluded that oppositely charged sols precipitate each other. Bechhold,[3] Neisser and Friedman,[4] Henri[5] and his coworkers, and Teague and Buxton,[6] published work confirming this rule. Spring[7] (1900), stated that upon mixing aniline blue (which migrates to the anode) and Magdala red (which migrates to the cathode), no precipitation occurred, which he thought disproved Lottermoser's work.

Lottermoser attempted to analyze the mixed gels, but because of absorption of excess colloid and other difficulties, quantitative results were impossible. Biltz[8] (1904) made a quantitative study of mutual precipitation by mixing measured quantities of sols which had been analyzed for the dispersed phases.

The following table is typical of the many giving his results:

2 cc. sol containing	13 cc. sol containing	Appearance	
		Immediately	After one hour
5.6 gr. Sb_2S_3	20.8 gr. Fe_2O_3	Turbid	Slight precipitation
"	12.8	Turbid	Slight precipitation
"	8.0	Slow settling	Complete precipitation
"	6.4	Complete precipitation	Complete precipitation
"	4.8	Incomplete precipitation	Incomplete precipitation
"	3.2	Slight precipitation	Unchanged
"	0.8	Slight precipitation	Unchanged

The ratio between precipitating sols varied so that the only conclusions that could be drawn were that there are certain proportions in which sols must be mixed for complete precipitation; outside of this range there is partial precipitation within certain limits, and if either sol is present in great excess no precipitation occurs. Spring's failure to obtain precipitation with the dyes of opposite migration in an electrical field was due to the proportions in which they were mixed.

In a comparison of precipitating values of the same sol against other sols as given in the following table from Biltz's work, he

showed that while the optimum amount of a positive sol to precipitate negative sols varied, the order was always the same.

Mg. of Negative Sol.		Mg. of Positive Sol.					
		Fe_2O_3	ThO_2	CeO_2	ZrO_2	Cr_2O_3	Al_2O_3
Au	14	3.0	2.5	4	1.6	0.3	0.1-0.2
As_2S_3	24	13	6	4	2.0	0.5	2.0
Sb_2S_3	32	32	20	11	6.5	3.0	2.0

There is undoubtedly an equivalence between the optimum amounts of sols for precipitation, but it is not an equivalence between the particles of the dispersed phases of the sols. Billitzer[9] (1905) suggested that the equivalence is electrical, since at maximum precipitation there was no migration in an electrical field, and on either side the migration was in the direction of the sol in excess. He thought the equivalence would not be exact because of variations in the size and numbers of particles and in the concentration of the sols.

The following table is typical of his results:

1 cc. of As_2S_3 sol contained 2.07 mg. of As_2S_3
1 cc. of Fe_2O_3 sol contained 3.036 mg. of Fe_2O_3

cc. As_2S_3	cc. Fe_2O_3	State	Migration in an electrical field
9	1	No change	Anodic
8	2	Slightly turbid	Anodic
7	3	Precipitate	Anodic
5	5	Precipitate	None
3	7	Nearly complete precipitation	None
2	8	Partial precipitation	Cathodic
0.2	9.8	Slightly turbid	Cathodic

Lottermoser[10] suggested in a paper published in 1910 that the equivalence may be that of the small amounts of peptizing electrolyte in the sol, and that the precipitation may be due to a chemical action between the peptizing agents, by which they are removed. To test this he mixed positive silver iodide sols peptized by silver nitrate and negative silver iodide sol peptized by potassium iodide. The results summarized in the following table indicate that the explanation holds for this precipitation at least. The quantities given are millimoles at maximum precipitation.

	Positive Sol		Negative Sol	
	AgI	$AgNO_3$	KI	AgI
1.....	0.21	0.052	0.055	0.22
2.....	0.22	0.055	0.05	0.20
3.....	0.225	0.009	0.01	0.245
4.....	0.245	0.010	0.017	0.18
5.....	0.27	0.009	0.01	0.04
6.....	0.24	0.01	0.007	0.033
7.....	0.038	0.007	0.01	0.24
8.....	0.040	0.010	0.008	0.196
9.....	0.115	0.01	0.01	0.24
10.....	0.115	0.01	0.007	0.17
11.....	0.225	0.009	0.01	0.115
12.....	0.24	0.01	0.008	0.088

Freundlich and Nathansohn[11] (1921-22) found that there is mutual reaction between sols of like charge as well as between sols of opposite charge. Mixtures of arsenic trisulfide sol and sulphur

sol (Odén) are very much more sensitive to electrolyte precipitation than either alone—and will precipitate each other. Both migrate to the anode in an electrical field. The precipitation must be due to the reaction between the hydrogen sulfide and a thionic acid which peptize the arsenic trisulfide and sulfur sols respectively. Other examples of mutual reaction between like charged sols are noted.

PURPOSE OF INVESTIGATION

The purpose of this investigation was the determination of the relation between the amounts of peptizing electrolytes of mutually precipitating sols at the point of maximum precipitation.

MUTUAL PRECIPITATION OF FERRIC OXIDE AND SILICIC ACID HYDROSOLS

The mutual precipitations studied were those of ferric oxide sol, which is peptized by ferric chloride and silicic acid sol peptized by sodium silicate; and ferric oxide sol peptized by ferric chloride and arsenic trisulfide sols peptized by hydrogen sulfide and by arsenious acid.

PREPARATION AND ANALYSIS OF SOLS

FERRIC OXIDE.

Preparation.

Ferric oxide sols were prepared by adding 2 molar ammonium hydroxide very slowly, by dropping from a burette, to 2 molar ferric chloride, which was vigorously stirred, until the precipitated ferric hydroxide ceased to peptize or "dissolve" easily. The sols, which were very dark in color, were dialyzed in collodion bags against distilled water until the desired degree of "purity" was reached.

Analysis.

Iron. 3 cc. of concentrated sulfuric acid was added to 25 cc. of sol and the solution evaporated to dryness on a hot plate. This was to insure removal of chlorine. The dried residue was dissolved in 150 cc. of water, 10 cc. of 18 molar sulfuric acid added, the solution passed through a Jones reductor and titrated with standard potassium permanganate. Correction was made for the reducing of a blank of sulfuric acid.

Chlorine by Volhard's method. 10 cc. of nitric acid prepared by diluting concentrated acid (Sp. gr. 1.42), from which all oxides had been removed, with an equal volume of water, was added to 50 cc. of the sol and allowed to stand in a dark cool place until the solution was clear. An excess of standard 0.1 molar silver nitrate was added, the silver chloride filtered off and the excess titrated with 0.1 molar potassium thiocynate using the iron as indicator.

To determine the effect of the varying amounts of iron as

indicator, the potassium thiocyanate was titrated against silver nitrate – both of about 0.1 molarity. Iron alum containing .01361 gr. of iron per cc. was used as indicator, with the following results:

cc. $AgNO_3$	cc. KCNS	cc. Alum
25.00	19.05	1.00
25.00	19.03	5.00
25.00	19.00	10.00
25.00	19.01	30.00
25.00	18.95	40.00

As the iron concentration in the experiments fell within the more concentrated range here, the variations were not enough to require correction by adding iron to a definite concentration.

The amount of iron as iron chloride was calculated from the chlorine and this subtracted from the total iron gave the iron from which ferric oxide was calculated.

No.	Fe(1=at. wt.)	Cl(1=at. wt.)	Moles $FeCl_3$	Moles Fe_2O_3	$Fe_2O_3/FeCl_3$
1.....	0.1054	0.02686	0.00895	0.0482	5.35/1
2.....	0.1127	0.03224	0.01075	0.0509	4.8/1
3.....	0.1064	0.02668	0.00889	0.0483	5.37/1
4.....	0.0623	0.01016	0.00338	0.0294	8.65/1
6.....	0.0401	0.00535	0.00178	0.0191	10.6/1
15.....	0.0533	0.01553	0.00518	0.0507	9.8/1
17.....	0.0360	0.00800	0.00267	0.0346	13./1
20.....	0.0275	0.00436	0.00145	0.0267	18.5/1
21.....	0.0378	0.00692	0.00230	0.0367	15.9/1
23.....	0.3517	0.00714	0.00238	0.0339	14.3/1

SILICIC ACID SOLS.

Preparation.

Silicic acid sols were prepared by dissolving water-glass (Sp. gr. 1.4) in about ten times its weight of water and partially neutralizing with hydrochloric acid. The sols became opalescent after a few hours' standing. There is a tendency to gel as the concentration increases, and the less sodium silicate that remains in proportion to the silicic acid, the greater this tendency is. Consequently, for very concentrated sols there must be a large amount of the peptizing agent. Dilution prevents the formation of the gel. The sodium chloride formed by action of the sodium silicate and hydrochloric acid was not removed because the silicic acid of the freshly prepared sols permeated both clay and collodion membranes. An older sol did not pass through the collodion membrane to any appreciable extent, but the sodium hydroxide formed by the hydrolysis of the sodium silicate diffuses through the membrane almost as readily as does the sodium chloride. As the peptizing agent is removed, the silicic acid starts to settle out and the remaining sol is quite unstable due to the small amount of sodium silicate left. The effect of the sodium chloride on the precipitation was studied and will be discussed later.

Analysis.

Silicic acid: A portion of the sol was evaporated to dryness after several cc. of 12 molar hydrochloric acid had been added to it. The residue was twice wet with hydrochloric acid and evaporated to dryness, after which it was washed free of chlorides and weighed as silicon dioxide.

Sodium silicate: A portion of the sol was diluted with four or five times its volume of water, making a total volume of one or two hundred cc., depending on the concentration of the sol. Ten cc. of concentrated sodium chloride was added to replace sodium hydroxide, which might be held in the dispersed phase, and the solution titrated with 0.1 molar hydrochloride acid, using phenolphthalein as indicator. After neutrality is apparently reached the solution becomes pink upon standing, and a few drops of acid are necessary to discharge the color. To avoid errors due to this, a check was run by adding an excess of acid and titrating with sodium hydroxide, the results checked within 2%, which is well within the error of the subsequent determinations of precipitation ratios.

Sodium chloride: The sodium chloride was calculated from the amount of hydrochloric acid added to the water glass to form the silicic acid sol.

As no definite formula can be given for the sodium silicate, the concentrations are expressed in terms of silicon dioxide for silicic acid and sodium hydroxide for the stabilizing sodium silicate.

Composition of silicic acid sols in moles per liter.

	SiO_2	NaOH	SiO_2:NaOH	NaCl
1.....	0.221	0.0327	6.7/1	0.091
2.....	0.208	0.0356	5.8/1	0.081
3.....	0.305	0.0294	10.4/1	0.142
4.....	0.437	0.135	3.5/1	0.111
5.....	0.186	0.0115	1.6/1	0.093

PROCEDURE

Varying amounts of one sol were run from a burette into hard glass bacteriological tubes of uniform diameter, clearness and about 20 cc. in volume. Equal volumes of the other sol were run from a pipette or burette into the tube as quickly and as quietly as possible to avoid mixing. The sols were mixed by inverting the tubes two or three times, with as little agitation as possible, so that the mixing was complete. This was sufficient for mixing if the tubes were not more than three fourths full and were revolved as they were inverted. The point of maximum precipitation could be clearly seen by successive stages, first the greatest cloudiness in the series, followed by the first separation of particles, and usually the first sediment. The last was frequently over a wider range than the first two stages as the precipitating zone widened rapidly. All observations were made immediately after mixing by holding the series of tubes against a clean or open window. Artificial light was found to be quite unsatisfactory, as was the light late in the afternoon or on a dark day.

Some series precipitated more easily than others, probably because of greater agitation. Vigorous shaking usually precipitated the whole series immediately. A tube of greater diameter than the others or of cloudy or marked glass appeared more cloudy and consequently was misleading. A few series were centrifuged, but the time required in placing them in the centrifuge and the power

to throw out the fine particles resulted in complete precipitation over a wide range.

To avoid errors due to an unclean tube or some other factor, three or four determinations were made in each instance.

The effect of dilution of the sols is given in Table I.

TABLE I.

Effect of dilution upon mutual precipitation.

cc. Fe_2O_3 sol No. 6	cc. SiO_2 No. 1	Precipitation Results	Millimoles HCl	Millimoles NaOH
1. (Dilution 1:0	1:10)			
5.3	1 to 10	All coagulated to solid		
2. (Dilution 1:10	1:50)			
5.3	3.0	Partial		
5.3	3.5	Almost complete		
5.3	4.1	Complete	0.00284	0.00268
5.3	4.5	Almost complete		
3. (Dilution 1:50	1:250)			
5.3	4.5	Partial		
5.3	4.8)	Complete		
5.3	5.1) 4.9	Complete	0.00057	0.00064
5.3	5.4	Partial		
4. (Dilution 1:100	1:250)			
10	4.7	Much slower		
10	5.0	1st to precipitate	0.00065	0.00053
10	5.3	Much slower		
10	5.6	Much slower		

The table shows that the dilution of mutually precipitating sols narrows and sharpens the zone of maximum precipitation, and that the variation in ratio between the sols varies no more than in successive experiments with the same dilution. If carried beyond certain dilutions coagulation is almost imperceptible or so slow that it is very difficult to determine. The dilutions used for the work were the greatest giving sharp precipitations. Very unstable sols show considerably different ratios with dilution. This will be discussed later.

To avoid possible differences due to order of mixing, the order was always reversed at least once.

Tables 2 and 3 give the data found in determining the points of maximum precipitation in typical cases of the 37 experiments cited in Tables 4, 5, 6 and 7.

TABLE II.

Mutual precipitation of silicic acid hydrosol No. 1 with ferric oxide hydrosol No. 20.

Dilutions—Fe_2O_3 sol = 1:25 SiO_2 sol = 1:200

(Ferris oxide sol added to silicic acid sol)

First test			Second test		
cc. Fe_2O_3 sol	cc. SiO_2 sol	Results	cc. Fe_2O_3 sol	cc. SiO_2 sol	Results
5.3	4.0	Partial precipitation	5.3	4.5	Partial later precipitation
5.3	5.0	First and heaviest precipitate	5.3	5.0)	
5.3	6.0	Partial precipitation	5.3	5.5)	First to precipitate
5.3	7.0	Only slightly cloudy	5.3	6.0	Partial later precipitation
cc.	cc.				

Conclusion: 5.2 cc. silicic acid sol with 5.3 cc. of ferric oxide sol gives maximum precipitation.

Silicic acid sol added to ferric oxide

cc. Fe_2O_3 sol	cc. SiO_2 sol	Results
5.3	4.8	Fourth to precipitate
5.3	5.0	Second to precipitate
5.3	5.2	First to precipitate
5.3	5.4	Second to precipitate
5.3	5.6	Third to precipitate

Calculations

Chlorine of ferric oxide sol	Sodium of silicic acid sol
25 | .004365	200 | .03274
.00016	.0001637
5.3	5.2
.000848	.000850

$\therefore$ Maximum precipitation is at 5.2cc. of silicic acid sol to 5.3cc. ferric oxide sol.

This is better agreement than in the average experiment.

TABLE III.

Mutual precipitation of silicic acid sol No. 1 and ferric oxide sol No. 17.

Dilution: ferric oxide sol = 1:50 silicic acid sol = 1:200

(Adding ferric oxide sol to silicic acid sol)

First test			Second test		
cc. Fe_2O_3 sol	cc. SiO_2 sol	Results	cc. Fe_2O_3 sol	cc. SiO_2 sol	Results
5.3	3.0	Cloudy	5.3	4.0	Cloudy
5.3	4.0	Slow precipitate	5.3	4.5	Third to precipitate
5.3	5.0	First to precipitate	5.3	5.0	Second to precipitate
5.3	6.0	Second to precipitate	5.3	5.5	First to precipitate
5.3	7.0	Slow precipitation	5.3	6.0	Third to precipitate
5.3	8.0	Cloudy			

$\therefore$ Maximum precipitation lies near 5.2 cc. of silicic acid sol and 5.3 cc. of ferric oxide sol.

Adding the silicic acid sol to the ferric oxide sol

cc. Fe_2O_3 sol	cc. SiO_2 sol	Results
5.3	5.0	Second to precipitate
5.3	5.3	First to precipitate
5.3	5.5	Third to precipitate
5.3	5.7	Slow precipitation
5.3	5.9	Slow precipitation

Calculations

Chlorine	Sodium
50 | .008001	200 | .0327
.0001600	.000164
5.3	5.2
.000840	.000850

TABLE IV.

Showing the ratio at maximum precipitation of silicic acid sol No. 1 to different ferric oxide sols.

No.	Fe_2O_3 sol Dilution	cc.	Milli-equivalents Chloride	Sodium	SiO_2 sol cc.	SiO_2 sol Dilution
1	1:100	10.0	0.00199	0.00151	4.6	1:100
2	1:100	5.3	0.00171	0.00124	3.8	1:100
3	1:100	10.0	0.00267	0.00180	5.5	1:100
4	1:100	10.0	0.00102	0.00112	3.5	1:100
6	1:100	10.0	0.00054	0.00065	5.0	1:250
15	1:50	5.3	0.00165	0.00155	9.5	1:200
17	1:50	5.3	0.00085	0.00085	5.2	1:200
20	1:25	5.3	0.00085	0.00085	5.2	1:200
21	1:25	5.3	0.00147	0.00164	10.0	1:200
23	1:25	5.3	0.00151	0.00155	9.5	1:200

TABLE V.

Showing the ratio at maximum precipitation of silicic acid sol No. 2 to different ferric oxide sols.

No.	Fe_2O_3 sol Dilution	cc.	Milli-equivalents Chloride	Sodium	SiO_2 sol cc.	SiO_2 sol Dilution
1	1:100	5	0.00134	0.00116	6.5	1:200
2	1:100	5	0.00161	0.00107	6.0	1:200
3	1:100	5	0.00133	0.00097	5.5	1:200
4	1:100	10	0.00102	0.00098	5.5	1:200
6	1:50	10	0.00107	0.00107	6.0	1:200
13	1:100	10	0.00155	0.00134	7.5	1:200
17	1:50	5	0.00080	0.00085	4.8	1:200
20	1:40	10	0.00109	0.00110	6.2	1:200
21	1:40	10	0.00175	0.00160	9.0	1:200
23	1:50	5	0.00071	0.00071	4.4	1:200

TABLE VI.

Showing the ratio at maximum precipitation of silicic acid sol No. 3 to different ferric oxide sols.

No.	Fe_2O_3 sol Dilution	cc.	Milli-equivalents Chloride	Sodium	SiO_2 sol cc.	SiO_2 sol Dilution
1	1:100	5	0.00134	0.00103	7.0	1:200
2	1:100	5	0.00161	0.00132	9.0	1:200
3	1:100	5	0.00133	0.00163	7.0	1:200
4	1:100	10	0.00101	0.00092	6.3	1:200
6	1:50	10	0.00107	0.00088	6.0	1:200
15	1:100	5	0.00075	0.00060	4.0	1:200
17	1:50	5	0.00080	0.00068	4.5	1:200
20	1:40	10	0.00109	0.00088	6.0	1:200
[illegible]	1:40	5	0.00082	0.00068	4.5	1:200
23	1:50	5	0.00071	0.00063	4.6	1:200

TABLE VII.

Showing the ratio at maximum precipitation of silicic acid sol No. 5 to different ferric oxide sols.

No.	Fe_2O_3 sol Dilution	cc.	Milli-equivalents Chloride	Sodium	SiO_2 sol cc.	SiO_2 sol Dilution
15	1:100	10.0	0.00155	0.00046	4.0	1:100
17	1:50	10.0	0.00160	0.00069	6.0	1:100
21	1:40	5.0	0.00083	0.00037	3.2	1:100
23	1:50	5.0	0.00072	0.00035	3.0	1:100

Silicic acid sol No. 4 was precipitated at different dilutions against ferric oxide sols No. 4, 6, and 20. No clear zones could be determined, but in every case the milli-equivalents of sodium exceeded the milli-equivalents of chloride.

The precipitating volumes checked within 10% in all cases except the very impure silicic acid sol No. 4.

To test the effect of the sodium chloride present upon the point of maximum precipitation 0.03 gr. of sodium chloride (an amount equal to 60% of the amount of sodium chloride already present in the sol), was added to silicic acid sol No. 2 (diluted 1:200), and the sol precipitated with several ferric oxide sols with the following results:

No.	Fe_2O_3 sol Dilution	cc.	Milli-equivalents HCl Chloride	NaOH Sodium	SiO_2 sol cc.	SiO_2 sol Dilution
4	1:100	10.0	0.00101	0.00099	5.5	1:200
6	1:50	10.0	0.00106	0.00099	5.5	1:200
15	1:100	5.0	0.00077	0.00068	3.8	1:200
20	1:40	10.0	0.00109	0.00107	6.0	1:200

It appears that the sodium chloride is without appreciable influence on the precipitation of silicic acid sols and ferric oxide sols in the experiment cited, and consequently no error was introduced by its presence in the silicic acid sols used.

TABLE VIII.

Showing the ratio of ferric chloride expressed in equivalents of hydrochloric acid to sodium silicate expressed in equivalents of sodium hydroxide in the thirty-seven precipitations of ferric oxide sol and silicic acid cited in the foregoing tables. The values are milli-equivalents of sodium hydroxide per 0.001 milli-equivalents of hydrochloride acid.

The sols are arranged in the order of their purity, the ratio of sodium silicate in terms of sodium hydroxide to silicon dioxide decreasing from left to right, and the ratio of ferric chloride to ferric oxide decreasing from top to bottom.

Silicic Acid Sols.

Number		4	2	1	3	5
Moles $NaOH/SiO_2$		1/3.5	1/5.8	1/6.7	1/10.4	1/16.1
Ferric oxide sols						
No.	Moles $FeCl_3/Fe_2O_3$					
2	1/ 4.8		0.00061	0.00073	0.00080	
1	1/ 5.35		0.00080	0.00055	0.00027	
3	1/ 5.37		0.00073	0.00069	0.00027	
4	1/ 8.65	> 100%	0.00096	0.00091	0.00090	
15	1/ 9.8		0.00090	0.00100	0.00080	0.00029
6	1/10.6	> 100%	0.00106	0.00094	0.00082	
17	1/13		0.00101	0.00090	0.00080	0.00043
23	1/14.3		0.00101	0.00091	0.00090	0.00048
21	1/15.9	> 100%	0.00098	0.00110	0.00080	0.00044
20	1/18.5		0.00093	0.00100	0.00080	
(Excluding 2, 1, 3)						
Average		> 100%	0.00098	0.00095	0.00083	0.00041

Table No. 8 shows that over a wide range of ratios between peptizing agent and dispersed phases of sols, there is a constant ratio between the peptizing agents of mutually precipitating sols and a very varying ratio between the dispersed phases. This leads to the conclusion that the precipitation is due to removal of the peptizing agents by a chemical action between them. As no definite formula can be given for the silicates it is impossible to express the reaction between sodium silicate and ferric chloride in an equation. However, the peptizing ferric chloride and sodium silicate can be given in terms of their hydrolysis products which are in equilibrium with the dispersed phase complexes, and consequently in the mutual precipitation of ferric oxide and silicic acid sols the reaction may be expressed as:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Another indication of such a reaction is given by the difference of hydrogen ion concentration in the supernatant liquid of precipitation of varying degrees. Varying amounts of silicic acid sols No. 3 (diluted 1:25) were added to 25 cc. of ferric oxide sol No. 4 (diluted 1:10), the precipitate allowed to settle and the hydrogen ion concentration of the supernatant liquid determined with the results given in Table 9. The ferric oxide sol is slightly acid, and the silicic acid sol distinctly alkaline to phenolphthalein as indicator.

TABLE IX.

Showing change in hydrogen ion concentration with varying precipitation of ferric oxide and silicic acid sols.

Silicic acid sol cc.	Precipitation	Negative log hydrogen ion concentration
10	Very slight	
	Excess of Fe_2O_3 sol	5.6
16	Maximum pption	6.8
18	2nd of series	7.8
20	Slow pption	> 8.3 (Alkaline to phenolphthalein)

Thus it is evident that maximum precipitation occurs at neutrality as the chemical equivalence of peptizing electrolyte demands and that the acidity increases with excess ferric oxide sol, and the alkalinity increases with excess silicic acid sol.

The ferric oxide sols, excluding Nos. 1, 2 and 3 (which contain the greatest amount of the peptizing agent in proportion to the dispersed phase), give a one to one ratio with silicic acid sols Nos. 1 and 2. With silicic acid sol No. 3, the same ferric oxide sols give a constant ratio with the ferric chloride of the same ferric oxide sols. As the sol becomes purer in respect to peptizing agent, it becomes more unstable and the precipitating ratios become more inconstant. This agrees with the general experience with "pure" ferric oxide sols. It is known that when a certain degree of "purity" is passed in a sol, the sol precipitates. The sol containing only a little more than the necessary minimum of peptizing agent is in a metastable condition, and the least disturbance will precipitate it. This may easily account for the ready precipitation of the pure ferric oxide sols.

The effect of diluting unstable sols in mutual precipitation is shown in the following table:

Precipitation of ferric oxide sol No. 17 with silicic acid sol No. 5 of varying dilution.

Dilution		Milli-equivalents		NaOH equivalents of HCl equivalents
SiO_2 sol	Fe_2O_3 sol	NaOH	HCl	
1:50	1:50	0.00057	0.00160	35%
1:100	1:50	0.00069	0.00160	43%
1:200	1:50	0.00080	0.00160	50%

This shows that the amount of peptizing agent in the sol at maximum precipitation increases with dilution. It is possible that this is due to a greater availability of the peptizing agent as suggested—or it may mean that upon greater degree of dilution, the particles are farther apart and there are less chances of collisions, as Kruyt and van der Spek have suggested to explain dilution effects.

Both ferric oxide and silicic acid sols show erratic results in precipitation, if they contain large amounts of peptizing agent. This is undoubtedly due to the fact that some of the peptizing agent has been absorbed in the coagulum and carried down with it.

INVESTIGATION OF FERRIC OXIDE SOL AND ARSENIC TRISULFIDE MUTUAL PRECIPITATION

The ferric oxide sols used in this work were the same as those used with silicic acid sols and the method of procedure was the same.

ARSENIC TRISULFIDE SOLS.

Preparation.

Hydrogen sulfide gas was passed into a warm solution of arsenic trioxide, which had been prepared by dissolving from five to ten grams of resublimed arsenic trioxide in a liter of boiling water. The water was boiled first to remove dissolved oxygen and the arsenic trioxide finely powdered to hasten solubility. It was necessary to boil for several hours to complete solution. The pep-

tizing agent was hydrogen sulfide passed in to excess and arsenous acid, when it was in excess.

Analysis.

Arsenic: The most exact method of the methods tried for arsenic was that of Fanelli[13]. Twenty-five cc. of nitric acid (Sp. gr. 1.4 ×) was added to an equal volume of sol, and the mixture boiled until the arsenic trisulfide was completely dissolved. The particles of sulphur were filtered off to prevent reduction of the arsenic and the solution evaporated to dryness on a hot plate to expel all nitric acid. The dry residue was dissolved in 40 cc. of hydrochloric acid of such a strength that the solution would be 6 molar in respect to the acid, when 10 cc. of a solution containing 2 or 3 grams of potassium iodide is added. Thirty seconds after adding the potassium iodide, the solution is diluted to 3 molar hydrochloric acid, and immediately titrated with 0.05 normal sodium thiosulfate solution.

Sulfur: Ten cc. of the concentrated alkali was added to 25 cc. of the sol and 1 cc. of bromine added to the solution. This was boiled almost to dryness to oxidize the sulfur to sulfate, dissolved in water, made acid with hydrochloric acid and precipitated as barium sulfate.

Calculating the arsenic trisulfide from the sulfur or the arsenic, depending upon which was there in the least chemical equivalents the amount of peptizing agent was calculated by difference between the arsenic trioxide or hydrogen sulfide in the arsenic sulfide, and the total shown by analysis.

Many attempts were made to drive over the excess hydrogen sulfide and thus determine it directly, but in every instance there was decomposition of the arsenic trisulfide. For example 100 cc. of sol containing only 1% of phosphoric acid (Sp. gr. 1.7) was completely dissolved by 15 minutes' boiling. This was surprising in view of the generally accepted ideas of the stability of arsenic trisulfide, and may be due to its fine division in the sol. At no time was there precipitation during the heating, unless electrolytes had been added to the point of precipitation.

Ward[14] states that at temperatures below 35 °C., the hydrogen sulfide can be driven off from arsenic sulfide without decomposition, but several attempts to remove only the hydrogen sulfide by passing carbon dioxide gas through the pure sol, or the sol precipitated by neutral sols, resulted in appreciable decomposition.

Quantitative determination of the peptizing hydrogen sulfide in a sol by difference between the total sulfur and the sulfur of the arsenic trisulfide is unreliable as shown by the following analysis of an arsenic trisulfide sol.

Moles H_2S = .04442 (per liter)
Moles As_2O_3 = .01448 (per liter)
Moles As_2O_3 x 3 = moles H_2S as As_2S_3 = .04344

.04442
.04344

.00098 moles of peptizing hydrogen sulfide

As_2S_3 : H_2S :: .014 : .001

Any error in the arsenic is multiplied by three in the H_2S and that error comes entirely from the peptizing electrolyte, which would be a considerable proportion of the peptizing hydrogen sulfide. Also any error from sulfur due to lack of complete oxidation (which is very difficult), or to absorption which is most likely, would be taken from or added to the sulfur in the peptizing agent varying that easily to as much as 100%.

The arsenic trisulfide sol was precipitated against a few of the ferric oxide sols, which gave a constant chemical equivalence with silicic acid sols. The petizing electrolytes were of the same order, but there was too great variation to draw any definite conclusion. This was not surprising, as any sols studied have given constant ratios only over certain ranges, and this could easily have been out of that range. The determination of a constant precipitating range is only accidental or requires a great number of experiments, and in view of the analytical restrictions it was felt that this did not justify the work required.

If there is an equivalent reaction, there would be

$$H_2S + 2\ FeCl_3 \longrightarrow 2\ FeCl_2 + S + 2\ HCl$$

with a possibility of

$$3\ H_2S + 2\ FeCl_3 \rightarrow 2\ FeS + S + 4\ HCl$$

In most precipitations there is no evidence of the latter reaction as the precipitate is yellow. If, however, the sol contains a great amount of the H_2S, there is a blackening which can be explained by the formation of ferrous sulfide.

The most probable ratio would be H_2S : $FeCl_3$ :: 1:2. From the calculations with the analysis of the arsenic trisulfide sol, it was more nearly H_2S : $FeCl_3$: 2:1, an abnormally high value for H_2S. This indicates strongly a high value of the sulfide, due to absorption of impurities by the $BaSO_4$.

To test the precipitate for sulfur, 500 cc. of the arsenic trisulfide was precipitated with ferric oxide sol No. 4, the precipitate dried and extracted for five hours with carbon bisulfide. For comparison 500 cc. of the sol was precipitated by aluminium sulfate, the precipitate dried and extracted with carbon trisulfide. Both extractions produced sulfur as was expected from the chance of oxidation of the hydrogen sulfide in the sol, which was an old one, when

standing, and of the precipitate during drying. The sol precipitated by the ferric oxide sol yielded about 30% more sulfur than that precipitated by aluminium sulfate. Considering the small amount of hydrogen sulfide present, this difference is an indication that such a reaction had taken place between the ferric chloride and arsenic trisulfide.

It has been generally considered that hydrogen sulfide is the stabilizing agent of arsenic trisulfide sols. In this investigation, it was found that sols that contained an excess of arsenious acid, either through decomposing the arsenic trisulfide and driving out some hydrogen sulfide, or by failure to add an equivalent or slight excess of the hydrogen sulfide for the arsenious acid in solution when preparing the sols, were very stable. They gave a sharp range of precipitation with the ferric oxide sols, if sufficiently dilute, and acted in every way as did the arsenic trisulfide sols peptized by hydrogen sulfide. They have the advantage of having a non-volatile peptizing agent, and one that does not oxidize as readily as does hydrogen sulfide, thus being more dependable for quantitative work. The arsenic trisulfide sols peptized by arsenious acid will probably be found more satisfactory for further quantitative work on the mutual precipitation of ferric oxide and arsenic trisulfide sols, than those peptized by hydrogen sulfide have been.

CONCLUSIONS

1. It is demonstrated that the precipitating ratios of certain mutually precipitating hydrosols depend upon the peptizing agent.

2. There is chemical equivalence between the peptizing agents of ferric oxide hydrosol peptized by ferric chloride, and silicic acid sols peptized by sodium silicate, provided the ratio of peptizing agent to the dispersed phase falls within a certain range. Outside of this range the precipitation is erratic.

3. Ferric oxide-silicic acid sol precipitations showing chemical equivalence between the peptizing agents at maximum precipitation show little variance in precipitation ratios with dilution, while those showing a divergence from chemical equivalence approach chemical equivalence with dilution.

4. Mutual precipitation of ferric oxide and silicic acid sols is due to the removal of peptizing agents by chemical reactions between them.

5. Qualitative experiment shows that the mutual precipitation of arsenious sulfide hydrosol and ferric oxide hydrosol may be due to the chemical reaction:

$$H_2S + 2\ FeCl_3 \longrightarrow 2\ FeCl_2 + S + 2\ HCl$$

It was impossible to verify this quantitatively due to analytical restrictions.

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